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A Convenient Protocol for the Synthesis of Ligands from a 4-Methyl-3,5-diacylaminophenyl Platform

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The synthesis of stable and highly organized phenanthroline, terpyridine, and pyridino-oxazoline ligands bearing one or two 4-methyl-3,5-diacylaminophenyl modules equipped with two lateral dialkoxyphenyl groups has been performed using EDC·HCl and DMAP reagents in the final coupling reaction. Evidently, in the final ligands and in the solid state intermolecular hydrogen bonding maintains the coherence of the tridimensional structure as clearly evidenced by FT-IR and X-ray diffraction spectroscopy in the cases of the methoxy ligands. The supramolecular packing is also maintained by additional $\pi-\pi$ stacking interactions.

Crystal engineering[1,2] based on hydrogen bonding as a mechanism of assembly has been the object of considerable interest over the past decade. Hydrogen bonds have the special attributes of being both directional and labile, the latter characteristic being important in that it renders "self-repair" processes possible.[3] Molecular aggregation through H-bonding is a familiar mechanism for the control of organic reactions[4,5] and has also been used for the engineering of organic liquid−crystalline, well-defined nano- or mesoscopic assemblies, thin films and polymeric materials that self-assemble from simple elementary units.[6,7] Hierarchical self-organization events involving hydrogen bonding are of significant importance not only for the formation of liquid−crystalline phases but also for the stabilization of existing mesophases.[8,9]

As gelators for organic solvents, *numerous H-bonding amides* including glutamate derivatives have proved particularly useful.[10,11] Some of the resultant gels appear to have great potential as functional soft materials.[12] Recently, the gelation of room-temperature nematic liquid crystals in low molecular weight molecules aggregated by hydrogen bonding has been reported, and this new class of liquid−crystalline materials has great potential in dynamic materials such as in electrooptic devices and as systems responsive to fast stimuli.[11,13]

Investigations of transition-metal-containing liquid crystalline material (metallomesogens) are severely limited by the tedious synthesis of adequate ligands bearing a well-balanced ratio between the central rigid core and the paraffin chains. In some cases, hydrogen-bonding or $\pi-\pi^*$ interactions favor the emergence of mesophases.[14] To further this approach, we sought to use a 4-methyl-3,5-diaminobenzoic ester platform. This choice was mo-

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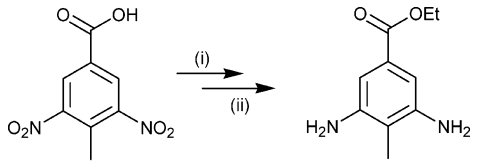
SCHEME 1 [a]

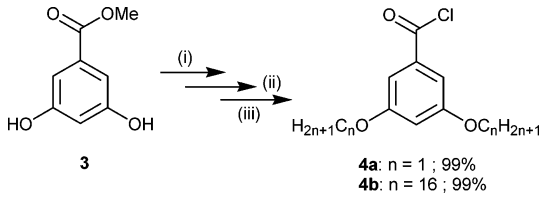


[a] Key: (i) H_2SO_4 (cat.), EtOH, reflux, 89%; (ii) H_2, Pd/C, EtOH/CH_2Cl_2, 99%.

tivated by the easy access to a diacylamino core where paraffin chains could be connected at the periphery of phenyl groups and a chelating fragment linked via the ester function to the central tetrasubstituted phenyl ring. The presence of a methyl group bisecting the central phenyl group is necessary to tilt the amide vectors out of the plane and so favor intermolecular hydrogen bonding in the ligand. Phenanthroline, terpyridine, and pyridino-oxaxoline substituents were considered of primary interest as chelating units because of their well-established capacity to bind transition metals, giving complexes with useful photochemical, redox and catalytic properties.[15] When embedded into organized mesophases such as columnar liquid crystals, they could provide the opportunity to transport charge, ions, and energy in photovoltaic or one-dimensional ion transport devices.[16] Recently, one-dimensional organic nanostructures were engineered in solution or self-assembled on gold surface from hexa-substituted phenyl rings incorporating three amido and three ether or ethynyl functions. This core motif allows the adjacent amide groups, although connected to the external phenyl rings via the amide nitrogens, to twist out of the place in order to favor intermolecular hydrogen bonding.[17]

In this paper, we report a protocol for the synthesis of a new class of ligands based on a diacylamino central core. The method is general and it allows for the convenient synthesis of a series of homologous ligands in which the nature of the chelating subunit and the length and the number of the greasy chains can be varied at will. The synthetic strategy requires preparing two pivotal starting materials depicted in Schemes 1 and 2. Preparation of ethyl 4-methyl-3,5-diaminobenzoate **2** requires a two-step protocol starting from commercially available 3,5-dinitro-*p*-toluic acid **1**. After esterification, the facile reduction of both nitro groups provides the first building block in excellent yield (Scheme 1). Also straightforward is the preparation of the 3,5-dialkyloxybenzoic chlorides. Alkylation of the 3 and 5 positions of commercially available methyl 3,5-dihydroxybenzoate, followed by a saponification step, enables subsequent conversion to the acid chlorides **4a/b** (Scheme 2). Species with other chain lengths can be prepared using the same protocol. Also feasible is an increase of the number of these chains by starting from trisubstituted gallic acid derivatives.

SCHEME 2 [a]



[a] Key: (i) 1-bromoalkane, K_2CO_3, MeCN, 100 °C, 99% for n = **16**; (ii) EtOH, KOH, reflux; then H_2O, HCl (10%), 92% for n = **16**; (iii) $SOCl_2$, reflux.

Using such starting materials, it was possible to covalently connect two peripheral alkyl/phenyl groups **4a/b** to a central ethyl 3,5-diamino-4-methylbenzoate **2** as outlined in Scheme 3. Double condensation of **4a/b** under stoichiometric reaction conditions provided compounds **5a/b** in good yields. Sodium carbonate was used to trap evolved hydrochloric acid, and acetone was used to precipitate the desired compounds after separation of the solid base and cooling the solution to −20 °C. The primary purpose in grafting peripheral phenyl groups onto the central ring was to increase the size of the rigid aromatic core.

A secondary purpose was to use them to anchor the aliphatic chains. To obtain mesomorphic compounds, it is necessary to favor microsegregation between rigid and flexible parts of the molecules during the heating cycle. In the compounds presently synthesized, it was anticipated that the aliphatic cores would be effectively in a molten state, engendering partial mobility in ordered structures such as columns, layers, or spheres. The amide entity was expected to stabilize the supramolecular networks within the mesophases through formation of intramolecular H-bonds.[18]

To graft chelating sites on the platforms **5a/b**, it was necessary first to hydrolyze the ethyl ester functions. Classical saponification conditions such as KOH/EtOH or HCl/EtOH were ineffective but the use of excess NaOH in a mixture of THF/water at reflux was ultimately found to be successful (Scheme 3). Controlled acidification then provided the expected acids **6a/b**.

To connect the 4-methyl-3,5-diacylaminophenyl platform to the chelating groups we chose to use hydroxymethyl-substituted phenanthroline, terpyridine, and pyridino-oxazoline compounds (Scheme 4). Initial results revealed that the bis-amide derivatives **6a**/**b** could not be properly transformed to the corresponding acid chlorides either in the presence of $SOCl_2$ or $(COCl)_2$. Only intractable mixtures of compounds were obtained. Thus, we chose to investigate the esterification step under mild conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC). This dehydrating agent, commonly used in peptide synthesis, is conveniently used for esterification reactions in the presence of 4-(dimethylamino)pyridine (DMAP).[19]

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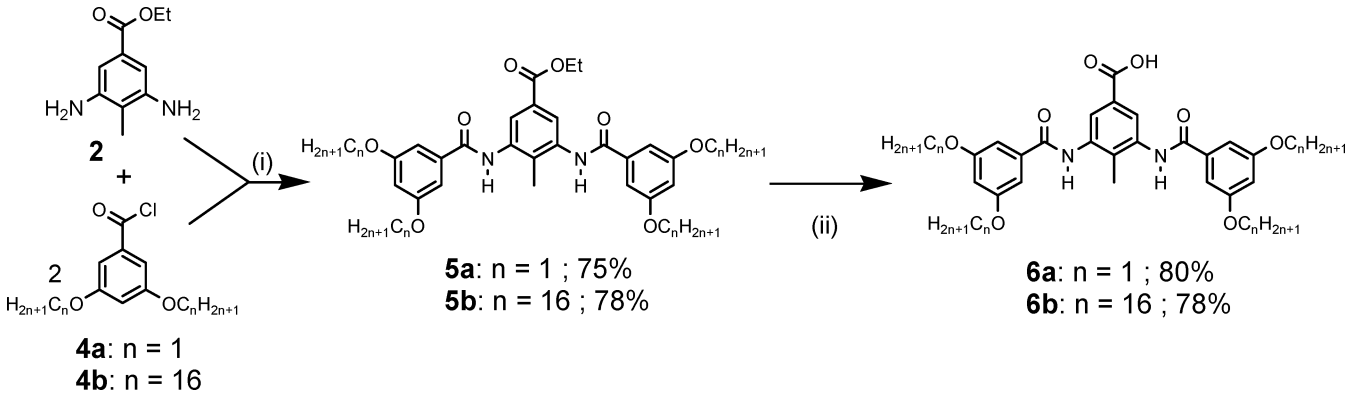
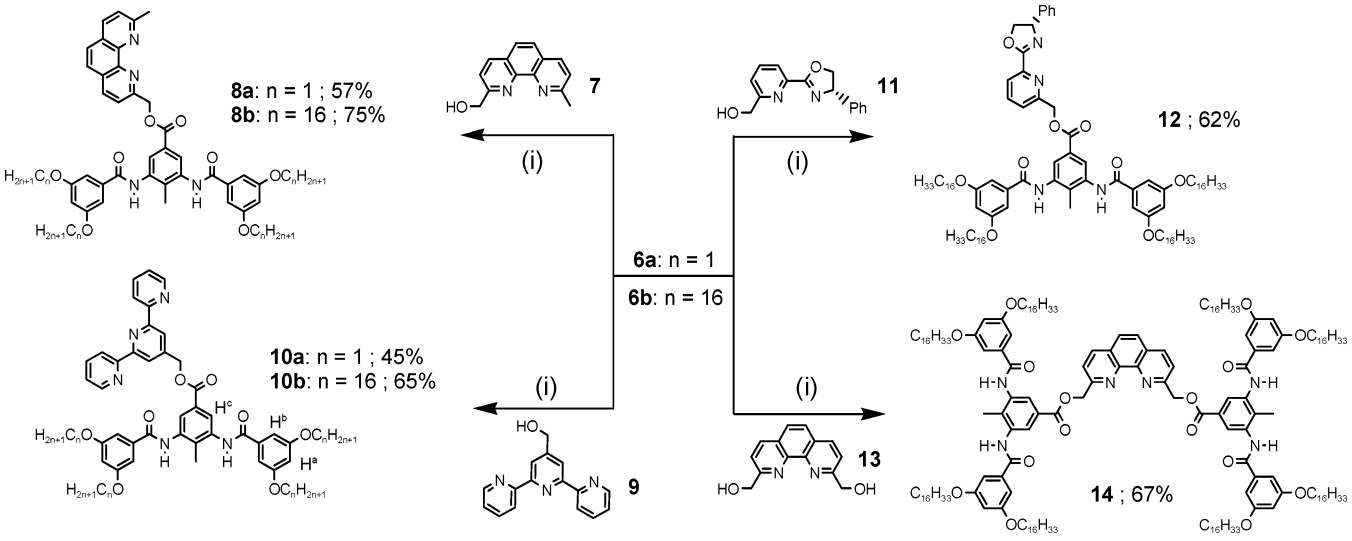
SCHEME 3 [a]



[a] Key: (i) anhydrous Na_2CO_3, acetone, reflux; (ii) NaOH (50 equiv), THF/H_2O (v/v), reflux; (iii) $CHCl_3$, HCl 10%.

SCHEME 4 [a]



[a] Key: (i) EDC·HCl (2 equiv for **7a/b**, **8a/b**, **9** and 4 equiv for **10**), DMAP (2 equiv), CH_2Cl_2/THF, rt.

Notably, 2-hydroxymethyl-1,10-phenanthroline coupled in excellent yield (>90%). However, a major drawback was that the *N,N′*-dicyclohexylurea coproduct could not be eliminated by multiple purification (chromatography and crystallization). Contamination of all the ester products was indicated by the presence of cyclohexane signals between 1 and 2 ppm in the ^{1}H NMR spectra. These peaks overlapped those of the aliphatic chain protons, resulting in integrals for these protons being apparently 25−50% too high. A simple solution to this problem was to use 1-ethyl-3-[3-(dimethylamino) propyl] carbodiimide (EDC·HCl),[20] as dehydrating agent. The target ligands were then isolated pure by column chromatography in acceptable yields (Scheme 4).

The ^{1}H NMR spectra of the final ligands display characteristic signals in the form of a triplet around 6.7−6.5 ppm, a doublet around 6.9−7.2 ppm, and a singlet at 7.9−8.1 ppm with integrals of 2, 4, and 2 (or 4, 8, and 4 for ligand **14**), respectively, for the phenyl protons H^a, H^b, and H^c (see Scheme 4 for labeling). The amide proton appears as a singlet at 8.2−8.7 ppm. The ester-bridge methylene signal appears as a singlet at 5.4−5.8 ppm and is insensitive to the nature of the chelating framework. The OCH_2 or OCH_3 groups (in the cases of **8a** and **10a**) were found as respectively a triplet and a singlet at 3.7 to 4.0 ppm. The methyl substituent of the tetrasubstituted central phenyl group was found in all cases at 2.1−2.2 ppm. All chelating fragments exhibit the expected patterns and chemical shifts. The FAB^+ mass spectra reveal the high stability of these ligands, with a major molecular peak corresponding to $[M + H]^+$ followed by fragmentation peaks due to the loss of the ester-chelate part of the molecule.

Infrared spectroscopy in the solid state supports the claim that strong intermolecular H-bonding is occurring in the solid state. FT-IR spectra recorded in $CHCl_3$ solution (at 9.3 mmol) revealed stretching vibrations for the amide at 3426 and 1677 cm^{-1} and a NH bending vibration at 1525 cm^{-1} for all ligands. These values lie in the expected range for a free amide function not involved in H-bonding.[21] In the solid state, major shifts are observed for ν_{NH} at 3224, ν_{CO} at 1644, and δ_{NH} at 1505

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cm^{-1}. In some cases, the bands split into two components of equal intensity. These results confirm that the amides are involved in tight hydrogen bonding in the solid state, whereas in solution no such evidence is obtained. Note that the $\nu_{C=C}$ of the aromatic rings around 1645 cm^{-1} and the ν_{COO} of the ester junction around 1720 cm^{-1} do not significantly change within the ligand series on switching from the solution to the solid state.

The unique coordination features of the bis-amide framework were confirmed by crystallographic structure determinations for ligands **8a** and **10a**. As expected, these ligands are nonplanar, the external trisubstituted rings being nearly perpendicular to the central tetrasubstituted phenyl ring. The phen and terpy subunits are tilted respectively by 68° and 64° relative to the central core (Figures 1a and 2a). The phen fragment is flat and in the *cisoid* conformation. The terpy unit is not planar; two pyridine rings (N1A and N1C) being tilted by 1.7°, while the third ring (N1B) is tilted out of the plane formed by the two other pyridines by 10.2°. The external pyridine rings adopts a *transoid* arrangement in order to minimize the electronic interaction between the neighboring nitrogen lone pairs. As anticipated from the original design, due to the presence of a methyl substituent bisecting the central tetra-substituted phenyl ring, the two amide-NH vectors point in opposite directions, which is auspicious for the formation of a polymeric H-bonded network between neighboring molecules. In the lattice of the phen ligand **8a**, two types of hydrogen bonds are apparent. For the shorter one, NH- - -O = 2.889 Å, while for the longer, NH- - -O = 3.012 Å. Both linkages form a zig-zag polymeric chain running along the *a* axis (Figure 1b). An additional feature which strengthens this chain is the $\pi-\pi$ stacking of the parallel aromatic cores shown by separations of 3.7 Å between L and L″ and 4.4 Å for subunits L and L′ (Figure 1b). In the lattice of the terpy ligand **10a**, two types of hydrogen bonds are seen again. The central hydrogen bond is shorter (NH- - -O 2.858 Å) compared to the phen, while the second is significatively longer (NH- - -O 3.097 Å). Both tethers generate a similar zig-zag chain running along the *a* axis (Figure 2b). Also present are stabilizing interactions between the almost parallel tetra-substituted phenyl rings (3.9 Å between L and L″ and 5.6 Å for subunits L and L′, Figure 2b).

In summary, we have shown that employment of a 4-methyl-3,5-diacylaminophenyl platform can provide an easy entry into novel oligopyridinic ligands bearing the necessary accessory to generate liquid crystalline materials. The key esterification step is made possible by the use of EDC·HCl as dehydrating agent. Evidently, in the final ligands and in the solid state, intermolecular hydrogen bonding as well as $\pi-\pi$ stacking interactions maintain the coherence of the three-dimensional structure as clearly shown in the phen and terpy cases **8a** and **10a**. Such supramolecular packing clearly stabilizes the lattice and may prove to be of value in controlling mesophase structures.

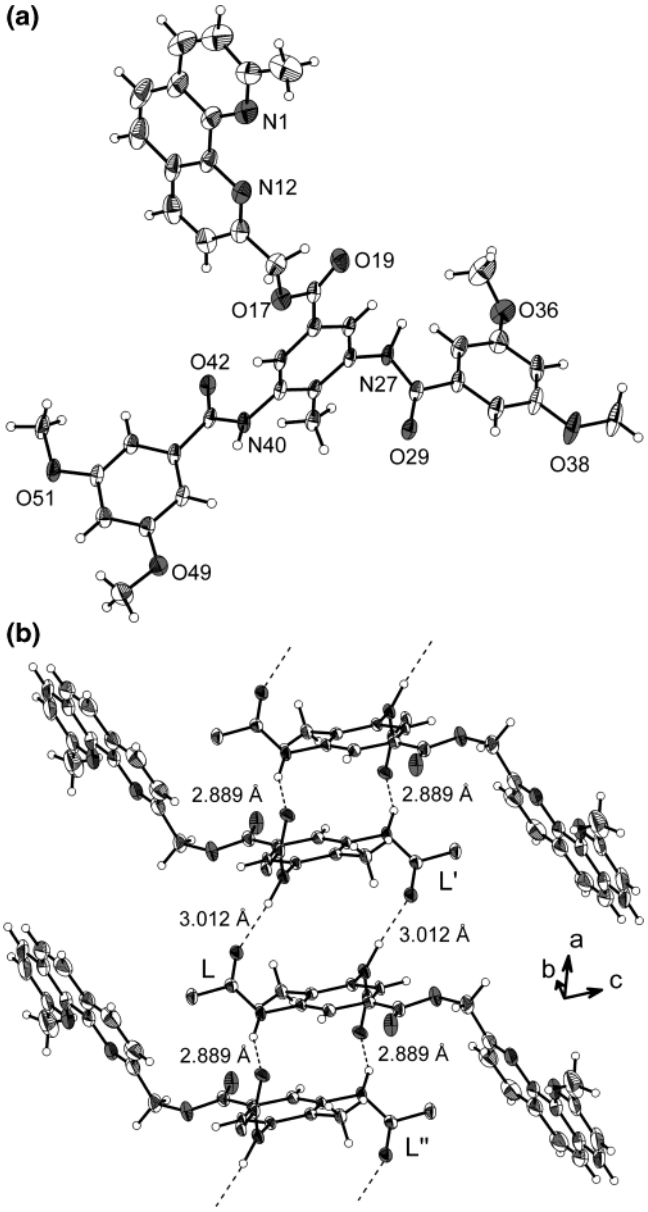

FIGURE 1. (a) Molecular structure of ligand **8a** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 30% level. (b) The hydrogen-bonding networks involving the amide groups are shown as broken lines. The hydrogen bonds connect centro-symmetrically the amide groups of L to L′ (NH- - -O = 3.012(3) Å, NHO angle 173(1)°), and L to L″ (NH- - -O = 2.889(3) Å, NHO angle = 156(1)°). For the sake of clarity, the two peripheral phenyl rings carrying the methoxy functions have been omitted.

Experimental Part

General methods were as described in a previous publication.[22] 2-(Hydroxymethyl)-9-methyl-1,10-phenanthroline **7**,[23] 4′-(hydroxymethyl)-2,2′;6′2″-terpyridine **9**,[24] (4′*R*)-2-(4′,5′-dihydro-4′-phenyl-2′-oxazolyl)-6-(hydroxymethyl)pyridine **11**,[25] and 2,9-bis(hydroxymethyl)-9-methyl-1,10-phenanthroline **13**[26] were prepared and purified according to literature procedures.

Ethyl 3,5-Diamino-4-methylbenzoate (2). To a solution of ethyl 3,5-dinitro-4-methylbenzoate (3.850 g, 15.14 mmol) in

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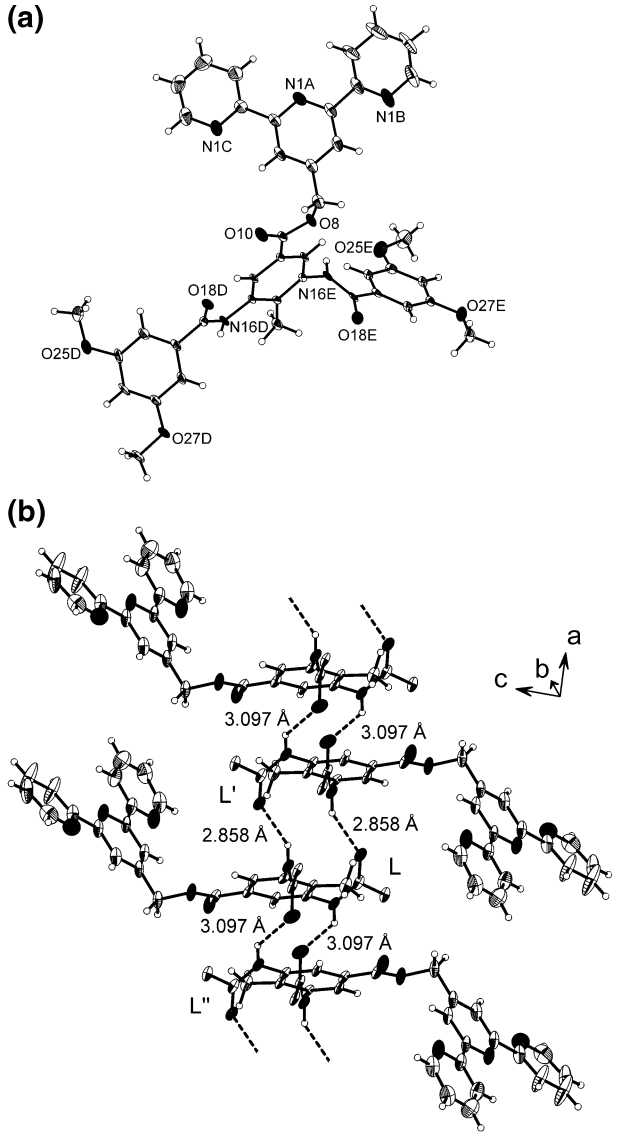

FIGURE 2. (a) Molecular structure of ligand **10a** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 30% level. (b) The hydrogen-bonding networks involving the amide groups are shown as broken lines. The hydrogen bonds connect centro-symmetrically the amide groups of L to L′ (NH- - -O = 3.097(3) Å, NHO angle = 135(1)°), and L to L″ (NH- - -O = 2.858(3) Å, NHO angle = 147(1)°). For the sake of clarity, the two peripheral phenyl rings carrying the methoxy functions have been omitted.

CH_2Cl_2/EtOH (50/50) was added 0.600 g of Pd/C, and the mixture was stirred with a dihydrogen inlet. After complete consumption of the starting material (determined by TLC), the excess of Pd/C was filtered out and the solvent evaporated to afford 2.9 g of **2** (99%). FT-IR (KBr pellets): 3368 (vs), 2980 (w), 1698 (s), 1626 (s), 1584 (s), 1431 (m), 1369 (m), 1343 (m), 1243 (s), 1204 (m), 1023 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.35 (t, ^3J = 7 Hz, 3H), 1.99 (s, 3H), 3.4 (m, 4H), 4.30 (q, ^3J = 7 Hz, 2H), 6.87 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 10.5, 14.3, 60.6, 107.4, 111.9, 128.8, 145.1, 167.0. FAB^+ *m/z* (nature of the peak, relative intensity): 195.3 ($[M + H]^+$, 100). Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.59; H, 6.94; N, 14.13.

3,5-Dimethoxybenzoic chloride (4a). A stirred suspension of 3,5-dimethoxybenzoic acid (2.090 g, 11.50 mmol) in thionyl chloride (15 mL) was heated at reflux until a clear solution had formed, after which the excess $SOCl_2$ was evaporated off and the resulting solid dried under vacuum to obtain 2.205 g of **4a** (96%) which was used without further purification. FT-IR (KBr cell): 2919 (s), 2853 (s), 1766 (m), 1590 (m), 1468 (m), 1324 (m), 1180 (m), 1076 (w), 950 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.84 (s, 6H), 6.74 (t, ^4J = 2.4 Hz, 1H), 7.24 (d, ^4J = 2.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 56.5, 109.2, 110.1, 134.5, 160.6, 168.9. FAB^+ *m/z* (nature of the peak, relative intensity): 201.1 ($[M + H]$, 100). Anal. Calcd for $C_9H_9O_3Cl$: C, 53.88; H, 4.52. Found: C, 53.62; H, 4.23.

3,5-Dihexadecyloxybenzoic Chloride (4b). The compound was prepared from 1.000 g (1.658 mmol) of 3,5-dihexadecylbenzoic acid and 10 mL of thionyl chloride to give 1.000 g of **4b** (99%). FT-IR (KBr cell): 2916 (vs), 2849 (s), 1764 (m), 1592 (m), 1463 (m), 1390 (w), 1314 (m), 1176 (m), 1136 (w), 1073 (w), 945 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (m, 6H), 1.25 (m, 52H), 1.78 (m, 4H), 3.97 (t, ^3J = 6.6 Hz, 4H), 6.73 (t, ^4J = 2.2 Hz, 1H), 7.21 (d, ^4J = 2.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.0, 29.1, 29.4, 29.6, 29.6, 29.7, 29.7, 32.0, 53.4, 68.6, 108.7, 109.5, 134.8, 160.4, 168.3. FAB^+ *m/z* (nature of the peak, relative intensity): 586.2 ($[M - Cl]$, 100). Anal. Calcd for $C_{39}H_{69}O_3Cl$: C, 75.38; H, 11.19. Found: C, 74.98; H, 10.88.

Ethyl 3,5-Bis(3,5-dimethoxybenzoylamino)-4-methylbenzoate (5a). To a stirred solution of **4a** (2.205 g, 11 mmol) in dry acetone (50 mL) were added **2** (0.854 g, 4.4 mmol) and Na_2CO_3 (2.330 g, 22 mmol), and the mixture was heated at reflux for 4.5 h. The excess Na_2CO_3 was filtered out from the hot solution and the diamide derivative was precipitated by cooling the filtrate at −20 °C. Purification was performed by crystallization from hot ethanol/$CHCl_3$ to afford 1.720 g of **5a** (75%). Mp: 216−217 °C. ^1H NMR ($CDCl_3$): δ 1.33 (t, ^3J = 7.2 Hz, 3H), 2.19 (s, 3H), 3.85 (s, 12H), 4.33 (q, ^3J = 7.2 Hz, 2H), 6.64 (t, ^4J = 2.1 Hz, 2H), 7.05 (d, ^4J = 2.1 Hz, 4H), 8.00 (s, 2H), 8.09 (s, 2H). ^{13}C NMR ($CDCl_3$): 13.4, 13.9, 14.7, 30.1, 56.1, 61.6, 104.6, 105.6, 124.1, 129.6, 132.2, 136.7, 161.5, 166.0, 166.30. FAB^+ *m/z* (nature of the peak, relative intensity): 523.2 ($[M + H]^+$, 100), 477.2 ($[M - OEt]$, 20). Anal. Calcd for $C_{28}H_{30}O_8N_2$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.13; H, 5.55; N, 5.21.

Ethyl 3,5-Bis(3,5-dihexadecyloxybenzoylamino)-4-methylbenzoate (5b). The compound was prepared from 0.130 g (1.66 mmol) of **4b**, 0.13 g (0.66 mmol) of **2**, 0.350 g (3.32 mmol) of Na_2CO_3, and 50 mL of dry acetone as described for **5a**, to give 0.705 g of **5b** (78%). Mp: 157−158 °C. FT-IR (KBr cell): 3293 (m, br), 2922 (vs), 2852 (s), 1718 (m), 1643 (s), 1593 (s), 1515 (m), 1462 (m), 1385 (w), 1345 (w), 1326 (w), 1263 (w), 1222 (w), 1161 (m), 1056 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (t, ^3J = 6.2 Hz, 12H), 1.25 (m, 104H), 1.33 (t, ^3J = 7.0 Hz, 3H), 1.78 (m, 8H), 2.21 (s, 3H), 3.98 (t, ^3J = 6.2 Hz, 8H), 4.33 (q, ^3J = 7 Hz, 2H), 6.63 (t, ^4J = 2.1 Hz, 2H), 7.01 (d, ^4J = 2.1 Hz, 4H), 7.90 (s, 2H), 8.11 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.6, 14.1, 14.2, 22.7, 26.1, 29.2, 29.4, 29.5, 29.7, 29.7, 32.0, 61.1, 68.3, 105.3, 105.7, 124.2, 128.4, 133.5, 136.0, 136.3, 160.5, 165.6, 166.3. FAB^+ *m/z* (nature of the peak, relative intensity): 1364.2 ($[M + H]^+$, 100), 1317.2 ($[M - OEt]$, 30). Anal. Calcd for $C_{88}H_{150}N_2O_8$: C, 77.48; H, 11.08; N, 2.05. Found: C, 77.42; H, 10.98; N, 1.99.

3,5-Bis(3,5-dimethoxybenzoylamino)-4-methylbenzoic Acid (6a). To a stirred solution of **5a** (0.650 g, 1.244 mmol, 1 equiv) in THF (75 mL) was added NaOH (2.500 g, 62.2 mmol, 50 equiv) in H_2O (75 mL), and the mixture was refluxed overnight. After evaporation of the THF, $CHCl_3$ was added to the mixture. Dilute HCl (26 mL, 50 equiv) was dropwise added, and the mixture was stirred for 2 h. After evaporation of $CHCl_3$, the desired compound precipitated from the aqueous phase and was isolated by filtration to afford 0.490 g of **6a** (80%). ^1H NMR ($CDCl_3$): δ 2.17 (s, 3H), 3.84 (s, 12H), 6.60 (t, ^4J = 2.1 Hz, 2H), 7.11 (d, ^4J = 2.1 Hz, 4H), 8.03 (s, 2H), 8.10 (s, 2H). FAB^+ *m/z* (nature of the peak, relative intensity) 495.3 ($[M + H]^+$, 100), 449.2 ($[M - COOH]$, 15). Anal. Calcd for $C_{26}H_{26}O_8N_2$: C, 63.15; H, 5.3; N, 5.66. Found: C, 62.85; H, 5.02; N, 5.47.

3,5-Bis(3,5-dihexadecyloxybenzoylamino)-4-methylbenzoic Acid (6b). The compound was prepared from 1.228 g (0.9 mmol) of **5b**, 1.800 g (45 mmol) of NaOH, and THF/H_2O (50/50) as described for **6a** to give 0.975 g of **6b** (81%). ^{1}H NMR ($CDCl_3$): δ 0.87 (m, 12H), 1.24 (br, 104H), 1.70 (br, 8H), 2.24 (s, 3H), 3.87 (m, 8H), 6.57 (t, ^4J = 2.1 Hz, 2H), 6.96 (d, ^4J = 2.1 Hz, 4H), 7.96 (m, 2H), 8.12 (m, 2H). FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1111.2 ([M + H]$^+$, 80), 1065.2 ([M − COOH], 20). Anal. Calcd for $C_{86}H_{146}N_2O_8$: C, 77.31; H, 11.01; N, 2.10. Found: C, 76.98; H, 10.74; N, 1.82.

Ligand 8a. A Schlenk flask equipped with a septum and an argon inlet was charged with **6a** (0.100 g, 0.202 mmol), 0.041 g (0.184 mmol) of 2-(hydroxymethyl)-9-methyl-1,10-phenanthroline **7**, 0.077 g (0.404 mmol) of EDC·HCl, 0.050 g (0.404 mmol) of DMAP, and distilled CH_2Cl_2/THF (20 mL/20 mL). The solution was stirred overnight. After evaporation of the solvent, the purification of the ligand was performed by flash chromatography on silica gel with CH_2Cl_2/methanol (100/0 to 99/1) as eluant, followed by crystallization from CH_2Cl_2/CH_3CN to afford 0.074 g of **8a** (57%). Mp: 272−273 °C. FT-IR (KBr): 3400 (shoulder), 3232 (m), 2940 (m), 2836 (m), 2358 (w), 1718 (m), 1649 (s), 1593 (vs), 1535 (shoulder), 1510 (s), 1456 (m), 1427 (m), 1350 (m), 1319 (s), 1251 (w), 1211 (vs), 1157 (s), 1105 (w), 1066 (m), 1045 (w), 999 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.19 (s, 3H), 2.78 (s, 3H), 3.81 (s, 12H), 5.75 (s, 2H), 6.72 (t, ^4J = 2.1 Hz, 2H), 7.17 (d, ^4J = 2.1 Hz, 4H), 7.66 (d, ^3J = 8.3 Hz, 1H), 7.85 (d, ^3J = 8;3 Hz, 1H), 7.94 (d, ^4J = 1.9 Hz, 2H), 7.97 (s, 2H), 8.38 (d, ^3J = 8.0 Hz, 1H), 8.53 (d, ^3J = 8.3 Hz, 1H), 8.68 (s, 2H). ^{13}C NMR (DMSO-d_6): δ 14.9, 25.9, 56.4, 68.8, 104.5, 106.5, 121.9, 124.6, 126.2, 126.2, 127.6, 127.7, 128.8, 137.0, 137.3, 138.0, 138.2, 138.4, 145.5, 156.5, 159.5, 161.3, 166.0. FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 701.2 ([M + H]$^+$, 100). Anal. Calcd for $C_{40}H_{36}N_4O_8$·H_2O: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.37; H, 5.08; N, 7.83.

Ligand 8b. The compound was prepared from 0.150 g (0.113 mmol) of **6b**, 0.025 g (0.113 mmol) of 2-(hydroxymethyl)-9-methyl-1,10-phenanthroline **7**, 0.043 g (0.226 mmol) of EDC·HCl, 0.014 g (0.113 mmol) of DMAP, and 30 mL of distilled CH_2Cl_2 to afford 0.130 g of **8b** (75%). Clearing point: 124 °C. FT-IR (KBr): 3400 (shoulder), 3224 (m), 2919 (vs), 2850 (s), 1720 (m), 1655 (shoulder), 1645 (s), 1593 (s), 1520 (shoulder), 1508 (m), 1465 (m), 1442 (m), 1384 (w), 1350 (w), 1321 (m), 1256 (w), 1217 (w), 1190 (vw), 1168 (s), 1056 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.87 (m, 12H), 1.25 (br, 104H), 1.71 (m, 8H), 2.14 (s, 3H), 2.86 (s, 3H), 3.90 (t, ^3J = 6.4 Hz, 8H), 5.69 (s, 2H), 6.56 (t, ^4J = 2.1 Hz, 2H), 7.06 (d, ^4J = 2.1 Hz, 4H), 7.48 (d, ^3J = 8.0 Hz, 1H), 7.60 (m, 3H), 8.10 (m, 4H), 8.43 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.9, 14.1, 22.7, 25.6, 26.0, 29.2, 29.4, 29.7, 31.9, 68.1, 68.3, 105.2, 105.7, 121.3, 123.8, 125.5, 126.5, 126.9, 128.1, 132.9, 136.1, 136.4, 136.7, 137.2, 145.2, 156.4, 159.5, 160.5, 165.3, 166.1. FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1542.6 ([M + H]$^+$, 100), 940.5 ([M − $C_{39}H_{70}NO_3$ + H]$^+$, 25). Anal. Calcd for $C_{100}H_{156}N_4O_8$·H_2O: C, 76.98; H, 10.21; N, 3.59. Found: C, 76.69; H, 10.05; N, 3.38.

Ligand 10a. A Schlenk flask equipped with a septum and an argon inlet was charged with the acid **6a** 0.050 g (0.101 mmol), 0.024 g (0.092 mmol) of 4′-(hydroxymethyl)-2,2′;6′2″-terpyridine **9**, 0.039 g (0.202 mmol) of EDC·HCl 0.022 g (0.202 mmol) of DMAP, and distilled CH_2Cl_2/THF (15 mL/15 mL). The solution was stirred overnight. After evaporation of the solvent, the purification of the ligand was performed by flash chromatography on silica gel with CH_2Cl_2/methanol (100/0 to 99/1) as eluant, followed by crystallization from CH_2Cl_2/CH_3CN to afford 0.031 g of **10a** (45%). Mp: 286−287 °C. FT-IR (KBr): 3400 (shoulder), 3259 (m), 2948 (w), 2834 (w), 2358 (m), 2331 (m), 1720 (m), 1666 (shoulder), 1647 (s), 1594 (vs), 1512 (s), 1461 (m), 1421 (w), 1348 (m), 1309 (s), 1249 (m), 1211 (s), 1155 (s), 1120 (w), 1068 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 3H), 3.73 (s, 12H), 5.42 (s, 2H), 6.50 (t, ^4J = 2.2 Hz, 2H), 6.98 (d, ^4J = 2.2 Hz, 4H), 7.3 (m, 2H), 7.83 (dt, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 2H), 8.12 (s, 2H), 8.32 (s, 2H), 8.57 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 14.1, 56.7, 68.5, 105.2, 105.6, 119.0, 120.0, 121.5, 123.9, 124.4, 127.6, 133.5, 136.0, 136.6, 136.9, 147.5, 149.4, 155.6, 155.3, 156.0, 160.2, 165.5, 166.6. EI-HRMS: calcd 739.772, found 739.773. Anal. Calcd for $C_{42}H_{37}N_5O_8$: C, 68.19; H, 5.04; N, 9.47. Found: C, 67.84; H, 4.82; N, 9.03.

Ligand 10b. The compound was prepared from 0.100 g (0.075 mmol) of **6b**, 0.018 g (0.068 mmol) of 4′-(hydroxymethyl)-2,2′;6′2″-terpyridine **9**, 0.028 g (0.149 mmol) of EDC·HCl,0.018 g (0.149 mmol) of DMAP, and 30 mL of distilled CH_2Cl_2 as described for **10a** to afford 0.070 g of **10b** (65%). Clearing point: 155 °C. FT-IR (KBr): 3400 (shoulder), 3270 (m), 2923 (vs), 2853 (s), 1726 (m),1661 (shoulder), 1644 (m), 1591 (s), 1525 (shoulder), 1511 (m), 1459 (m), 1407 (w), 1384 (w), 1348 (w), 1267 (w), 1220 (w), 1163 (s), 1051 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.87 (t, ^3J = 6.7 Hz, 12H), 1.25 (m, 104H), 1.69 (m, 8H), 2.13 (s, 3H), 3.85 (t, ^3J = 6.4 Hz, 8H), 5.41 (s, 2H), 6.50 (t, ^4J = 1.9 Hz, 2H), 6.96 (d, ^4J = 1.9 Hz, 4H), 7.29 (m, 4H), 8.10 (s, 2H), 8.31 (s, 2H), 8.57 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 13.0, 14.0, 14.1, 22.5, 22.7, 26.0, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9, 53.4, 65.0, 68.3, 105.0, 105.7, 118.9, 119.1, 121.4, 123.9, 124.2, 127.8, 133.7, 136.1, 136.8, 136.8, 147.1, 149.0, 155.5, 155.6, 155.9, 160.3, 165.2, 166.5. FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1581.2 ([M + H]$^+$, 100), 1317.2 ([M − terpyCH_2O + H]$^+$, <5). Anal. Calcd for $C_{102}H_{157}N_5O_8$: C, 77.47; H, 10.01; N, 4.43. Found: C, 77.32; H, 9.91; N, 4.29.

Ligand 12. A Schlenk flask equipped with a septum and an argon inlet was charged with 0.110 g (0.082 mmol, 1 equiv) of the acid **6b**, distilled CH_2Cl_2, and 0.020 g (0.165 mmol, 2 equiv) of DMAP, and the mixture was stirred until complete solubilization of the acid. Finally, 0.031 g (0.165 mmol, 2 equiv) of EDC·HCl and 0.020 g (0.075 mmol, 0.9 equiv) of (4′*R*)-2-(4′,5′-dihydro-4′-phenyl-2′-oxazolyl)-6-(hydroxymethyl)pyridine **11** were added to the solution, which was stirred overnight. After evaporation of the solvent, the purification of the ligand was performed by flash chromatography on silica gel with CH_2Cl_2/methanol (100/0 to 99/1) as eluant, followed by crystallization from CH_2Cl_2/CH_3CN to afford 0.073 g of **12** (62%). Clearing point: 131 °C. FT-IR (KBr): 3218 (w), 2918 (vs), 2848 (s), 1720 (m), 1647 (m), 1590 (s), 1519 (m), 1452 (s), 1330 (m), 1216 (m), 1162 (s), 1053 (w), 844 (w), 756 (w), 696 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.87 (t, ^3J = 6.7 Hz, 12H), 1.25 (m, 104H), 1.78 (m, 8H), 2.25 (s, 3H), 3.98 (t, ^3J = 6.7 Hz, 8H), 4.39 (t, ^3J = 8.4 Hz, 1H), 4.89 (dd, ^3J = 8.6 Hz, ^2J = 1.8 Hz, 1H), 5.43 (dd, ^3J = 8.6 Hz, ^2J = 1.8 Hz, 1H), 5.57 (s, 2H), 6.62 (t, ^4J = 2.1 Hz, 2H), 7.00 (d, ^4J = 2.1 Hz, 4H), 7.30 (m, 5H), 7.56 (d, ^3J = 7.8 Hz, 1H), 7.80 (t, ^3J = 7.8 Hz, 1H), 7.88 (d, ^3J = 7 Hz, 1H), 8.09 (s, 2H), 8.25 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 13.8, 14.1, 22.7, 26.05, 29.2, 29.4, 29.4, 29.6, 29.7, 29.7, 29.7, 31.9, 67.1, 68.4, 70.3, 105.4, 105.6, 123.4, 123.6, 123.8, 126.9, 127.8, 128.2, 128.8, 136.1, 136.6, 137.6, 141.7, 146.2, 156.4, 160.6, 163.7, 165.1, 166.1. FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 1572.1 ([M + H]$^+$, 100), 1320.1 ([M − pyoxCH_2O]$^+$, 20). Anal. Calcd for $C_{101}H_{158}N_4O_9$: C, 77.15; H, 10.13; N, 3.56. Found: C, 76.84; H, 9.92; N, 3.43.

Ligand 14. A Schlenk flask equipped with a septum and an argon inlet was charged with the acid **6b** (0.200 g, 0.149 mmol), 0.018 g (0.075 mmol) of 2,9-(hydroxymethyl)-1,10-phenantroline **13**, 0.115 g (0.6 mmol) of EDC·HCl, 0.019 g (0.15 mmol) of DMAP, and 30 mL of distilled CH_2Cl_2. The solution was stirred overnight. After evaporation of the solvent, the purification of the ligand was performed by flash chromatography on silica gel with CH_2Cl_2/methanol (100/0 to 99/1) as eluant followed by crystallization from $CHCl_3$/CH_3CN to afford 0.145 g of **14** (67%). Mp: 215−216 °C. FT-IR (KBr): 3436 (shoulder), 3247 (m), 2922 (vs), 2852 (s), 1737 (w), 1654 (shoulder), 1645 (m), 1595 (s), 1525 (shoulder), 1511 (w), 1455 (w) 1443 (m), 1384 (m), 1351 (w), 1319 (w), 1260 (w), 1215 (w), 1167 (s), 1058 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.87 (m, 24H), 1.24 (m, 208H), 1.67 (m, 16H), 2.09 (s, 6H), 3.85 (m, 16H), 5.54 (s, 4H), 6.53 (t, ^4J = 1.9 Hz, 4H), 7.01 (d, ^4J = 1.9 Hz, 8H), 7.69 (m, 4H), 8.02 (s, 4H), 8.19 (d, ^3J = 8.3 Hz, 2H), 8.46 (m,

4H). ^{13}C NMR ($CDCl_3$): δ 13.9, 14.1, 22.7, 26.0, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8, 32.0, 67.7, 68.3, 105.2, 106.8, 122.5, 123.9, 126.5, 127.5, 128.3, 133.4, 136.1, 136.6, 137.1, 145.1, 156.2, 160.3, 165.3, 166.1. FAB$^+$ *m*/*z* (nature of the peak, relative intensity): 2875.2 ($[M + H]^+$, 100). Anal. Calcd for $C_{186}H_{300}N_6O_{16}\cdot 2H_2O$: C, 76.71; H, 10.52, N, 2.89. Found: C, 76.53; H, 10.21, N, 2.67.

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Supporting Information Available: CIF files for the X-ray structures of compounds **8a** and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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